

## **Chapter Two**

### **Ephemeral acid mine drainage at the Montalbion silver mine, north Queensland**

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#### **2.1 Introduction**

Mining of metallic ore deposits may expose sulphide minerals to the atmosphere or oxygenated ground water. As a consequence, the sulphides will oxidise to produce an acid water laden with sulphate, heavy metals and metalloids. In particular, the weathering of pyrite at mine sites causes the largest, and most testing, environmental problem facing the industry today – AMD (Evangelou, 1995b; Lottermoser, 2003).

AMD is known to occur under all climatic conditions ranging from arctic to tropical. Much of the previous AMD research has focused on temperate regions in the northern hemisphere where sulphide oxidation in a wet climate produces a continuous supply of acid mine water. In contrast, vast regions of Australia are characterised by an arid or semi-arid climate and here, AMD generation only occurs when seasonal or irregular rainfall favours the infiltration of water into sulphidic materials and drainage is possible from sulphidic materials. In the seasonally wet-dry climate of northern Australia, sulphidic materials are exposed to an irregular wet-dry cycle, which may lead to ephemeral AMD. At the onset of the wet season, sulphide oxidation and mineral dissolution processes will generate AMD waters that may enter local surface waters and aquifers. Changing redox conditions commonly lead to the formation of Fe-rich precipitates (i.e. “ochres” or “yellow-boy”). Upon return to the dry season, AMD from the sulphidic material will cease. Evaporation causes the formation of

mineral efflorescences (i.e. post-mining minerals that form due to evaporation as surface encrustations; cf. Jambor et al., 2000) in pore spaces of sulphidic rocks, on stream beds and at seepage points and surfaces of waste rock dumps, ore stockpiles and tailings repositories. In such environments, the nature and occurrence of the secondary minerals are important because soluble or metastable minerals may store metals, metalloids, sulphate and acidity until the next rainfall event (Alpers et al., 1994b; Cravotta, 1994; Keith et al., 1999; Nordstrom and Alpers, 1999a; Bigham and Nordstrom, 2000; Jambor et al., 2000). Despite the knowledge that mineral efflorescences may impact on or even control the aqueous chemistry of AMD affected streams, much of the previous work on AMD has focused on sulphide oxidation processes (e.g. Evangelou, 1995b). In comparison, the characteristics and properties of ochres and mineral efflorescences are still poorly understood.

This chapter documents the environmental geochemistry and mineralogy of the abandoned Montalbion silver mine, north Queensland. The mine site is located in a semi-arid tropical environment and is characterised by ephemeral AMD. Particular emphasis is placed on the varied and unusual efflorescent mineral assemblage, which has an important control on the aqueous mobility of elements from the Montalbion mine site.

## **2.2 Montalbion mining area**

### **2.2.1 Physiography and climate**

The Montalbion mine site is located in north Queensland, 100 km southwest of Cairns and 7 km west northwest of Irvinebank on the western slopes of the Atherton Tablelands at latitude 17°24.4'S, longitude 145°08.4'E (Fig. 2.1). The mine site lies on an east-west trending hill rising steeply above Oakey Creek which is a tributary of the Walsh River. The region has a tropical savannah type climate with an average annual rainfall of 756 mm, 80 % of which falls between November and April (Dimbulah weather station, 30 km north of Montalbion)

(Bureau of Meteorology, 2003). Rainfall tends to be irregular and patchy, characterised by local storms and rare cyclonic downpours.

### 2.2.2 Local geology

The Montalbion silver lodes are hosted by the Hodgkinson Province, a regionally extensive Early to Mid Palaeozoic succession comprised of turbiditic sedimentary rocks with generally subordinate interlayered cherts, limestones and basic volcanic rocks (Bain and Draper, 1997; Garrad and Bultitude, 1999). At Montalbion, the mineralisation is enclosed by massive arenites with minor shales and siltstones which have been variably altered (Woodward, 1976). Alteration consists of extensive silicification and kaolinisation with isolated intensive sericitisation. The mineralisation is contained within narrow, steeply dipping, lenticular and pipe shaped quartz–sulphide veins. The ore lodes contain major amounts of galena, argentiferous tetrahedrite, sphalerite, chalcopyrite and pyrite, traces of pyrrhotite and marcasite, and a gangue of quartz, dickite and illite with minor sericite and siderite (Woodward, 1976). The mineralisation is also known for its elevated In concentrations. The lodes have been oxidised to a depth of at least 20 m, which has resulted in the widespread development of secondary sulphides (chalcocite, covellite), (hydr)oxides (goethite, hematite) and sulphates (anglesite, chalcantite, goslarite, plumbojarosite) (Dash et al., 1991). The mineralisation style was interpreted by Woodward (1976) as epithermal, formed by hydrothermal solutions sourced from nearby Mid to Late Carboniferous granites of the O’Briens Creek Supersuite.

### 2.2.3 Mine history

The region contains historically significant areas of mineralisation for a range of metals (Sn, W, Mo, Ag, Au, Cu, Pb, Zn, Sb) and the Montalbion mine site is located in one of the most intensively mined areas of Queensland (Dash et al., 1991). The Montalbion silver-lead lodes were discovered in 1885 and were mined between 1885 and 1895 by open cut and underground methods, producing 49 258 kg Ag and 1038 t Pb from 39 799 t of sulphide ore (Garrad

and Bultitude, 1999). Intermittent small-scale mining of unknown production quantities occurred until 1922 and several small sulphidic waste rock piles remain. The mine workings and waste dumps have remained undisturbed since 1922, with the exception of minor earthworks associated with mineral exploration in the 1970s (Woodward, 1976).

#### 2.2.4 Site description

The lodes occur in steep country, with slopes locally up to 30° and at altitudes between 620 and 800 m (Fig. 2.2a). Ground disturbed by mining activities covers an area of approximately 0.25 km<sup>2</sup> and includes a series of shafts, adits, pits, access tracks and waste dumps scattered across an east-west trending hill rising steeply above Oakey Creek (Fig. 2.1). In the mined areas, waste materials were dumped on steep slopes resulting in masses of unconsolidated mine waste extending down slope (Fig. 2.2a). The Rio Tinto waste dump is the largest, covering 13 000 m<sup>2</sup> with a vertical extent of 80 m (Fig. 2.1). Landsliding of the waste dumps continues especially during and after rainfall events. The actively eroding waste dumps are composed of diverse materials ranging from silty particles of less than 1 mm to boulders 0.5 m across. Constituents include metasedimentary material as well as minor sulphide fragments, pre- and post-mine oxidation minerals, and assorted mining waste. Uncontrolled, dynamic landsliding of the sulphidic material allows continuous oxidation of the waste. Little vegetation exists on the waste dumps and gullies draining the mine site are devoid of vegetation. Ephemeral drainage from the mine site, in particular the Rio Tinto dump, runs into ephemeral Oakey Creek, which has strong flow only after heavy rainfall and permanent waterholes during dry periods. Drainage from the Rio Tinto dump appears to be the only source of surface water to Oakey Creek during the dry periods. Where AMD waters from the Rio Tinto dump enter Oakey Creek, the aquatic and bankside plant communities disappear. Moreover, there are abundant Fe-rich, yellow-red-brown, gelatinous precipitates coating the streambed and floating in shallow water pools, and mineral salt encrustations on the stream bank and bed. These visible effects of AMD pollution continue for approximately 800 m downstream, where the stream

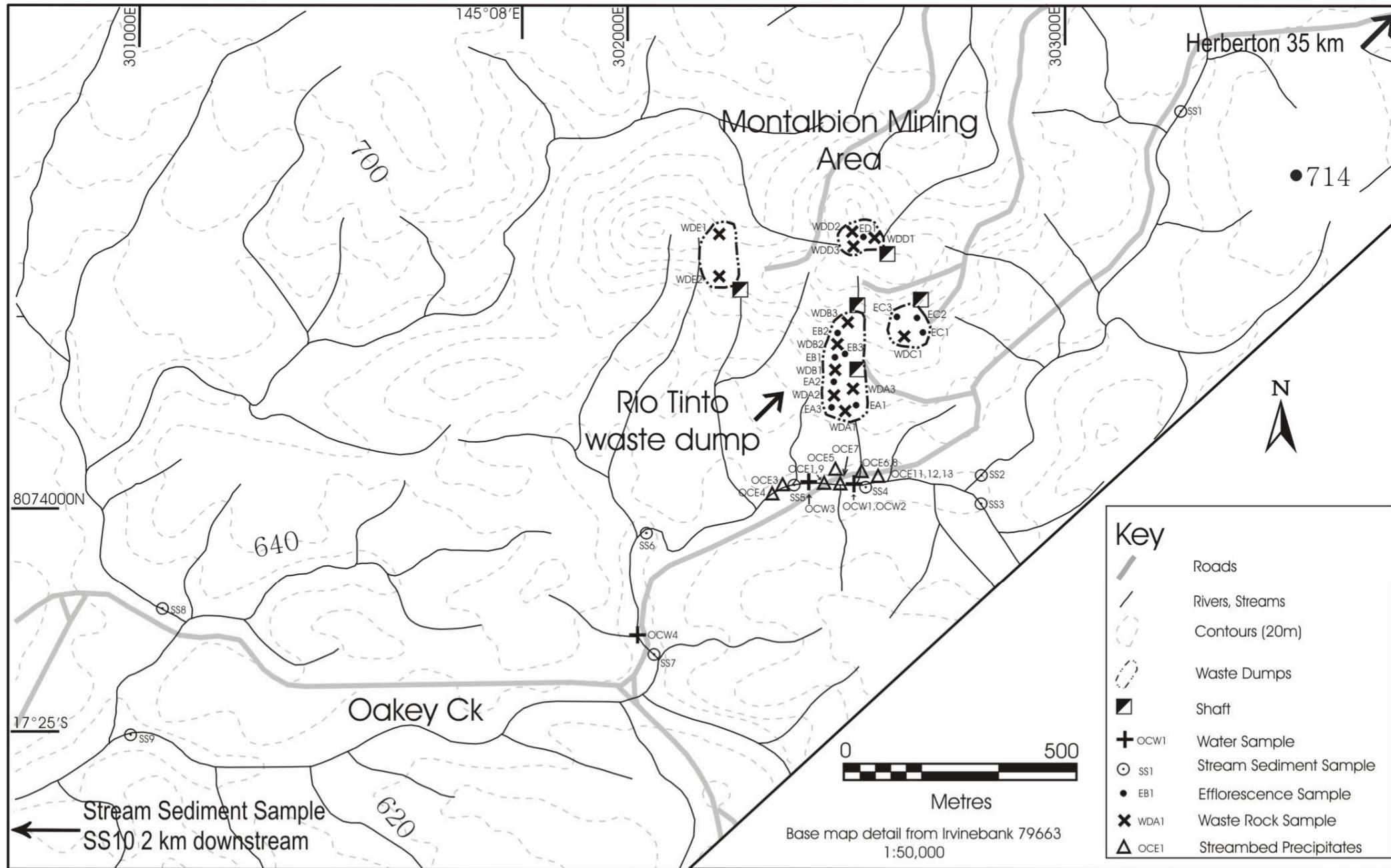


Figure 2.1. Montalbion mining area location map and sample location map showing waste dumps and Oakey Creek.

progressively recovers to exhibit a more typical aquatic ecosystem with diverse plant species and near neutral pH waters.

## **2.3 Materials and methods**

### **2.3.1 Sampling and sample preparation**

Field work was undertaken during June and September 2001 and April 2002. Over 60 stream sediment, water, Fe-rich precipitate, mineral efflorescence and mine waste samples were collected in the Montalbion area (Fig. 2.1) (sample locations listed in Appendix A1). Local background stream sediments were taken upstream of the Montalbion mine site. All solid samples were air-dried. The stream sediment samples were sieved to less than 150  $\mu\text{m}$  and less than 2 mm resulting in two size fractions (150  $\mu\text{m}$  to 2 mm; <150 $\mu\text{m}$ ). The two size fractions were chosen to evaluate physical dispersion of metals from the Montalbion mining area into Oakey Creek. Mine waste samples (~5 kg) comprised random grab sample composites and were taken from traverses across waste dump faces. Iron-rich precipitates were collected as grab samples from the Oakey Creek streambed. Mineral efflorescences were scraped from Oakey Creek sediments, adit walls and loose rocks on the waste dumps. Mine waste samples were crushed in a jaw crusher and ground in a chrome-steel mill, whereas mineral efflorescences and Fe-rich precipitates were ground with mortar and pestle in preparation for chemical and mineralogical analysis.

### **2.3.2 Mineralogical and geochemical analyses**

Powders of stream sediments, Fe-rich precipitates and mine wastes were dissolved in a hot HF-HNO<sub>3</sub>-HClO<sub>4</sub> acid mixture and analysed by inductively coupled atomic emission spectrometry (ICP-AES) for Ag, As, Bi, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Sb, W and Zn, and by inductively coupled plasma mass spectrometry (ICP-MS) for Be, In, Se, Sn, Te, Tl and U at Australian Laboratory Services Chemex, Townsville. Duplicate samples and an

aliquot of the geochemical reference material GXR-3 were used for data quality control.

Mineral identification of waste dump, stream sediment, Fe-rich precipitate and efflorescence samples was performed at the James Cook University (JCU) Advanced Analytical Centre (AAC) using X-ray diffraction (XRD) and quantitative computational software (SIROQUANT, EVA). Computational results were cross-checked using Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files. Scanning electron microscope (SEM) observations and energy dispersive spectrometry (EDS) measurements were conducted on representative Fe-rich precipitates and efflorescences at the JCU AAC. The qualitative mineral chemistry of selected sulphides was determined using a JEOL JXA840A electron microprobe (JCU AAC). Microprobe analyses were performed on major mineral efflorescences present in Oakey Creek using a Cameca SX-100 (Laval University, Quebec City, Canada). The microprobe analyses are regarded as semi-quantitative because porous sample materials returned excessive total element values compared to published halotrichite-dietrichite chemistries.

Water samples were collected for analysis of major cations and anions (waters unfiltered) and dissolved metals (waters filtered below 0.45  $\mu\text{m}$ ). Conductivity and pH were determined in the field. Chemical analyses were conducted by the JCU Australian Centre for Tropical Freshwater Research using argentometric titration ( $\text{Cl}^-$ ), potentiometric titration ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ), turbidometric spectrophotometry ( $\text{SO}_4^{2-}$ ), atomic absorption spectrometry (AAS) for major cations (Ca, K, Mg, Na) and ICP-MS for dissolved trace elements (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, In, Mn, Mo, Ni, Pb, Sb, Se, Zn). The PHREEQC2 modelling program (Parkhurst and Appelo, 1999) was used to establish the mineral phases in equilibrium with Oakey Creek and mine drainage waters.

### 2.3.3 Laboratory experiments

Paste pH measurements were performed on powdered mine wastes following the procedure of Morin and Hutt (1997). In addition, three representative mine waste materials from the Rio Tinto dump were subjected to short-term kinetic dissolution experiments. The experiments aimed (a) to curtail sulphide oxidation in the waste samples, and (b) to establish whether the dissolution of secondary minerals influences the chemistry of 'first flush' drainage waters emanating from the Rio Tinto waste dump. The waste samples (200 g of a 2-20 mm size fraction) were completely immersed in distilled water for a period of one day, one week and one month. All water was removed after one day and after one week. The mine wastes were then re-immersed in freshly distilled water. Conductivity and pH values of the leachates were measured at the conclusion of each time interval. The one day, one week and one month old leachates were submitted for chemical analysis using ICP-MS methods (Al, As, Ca, Cd, Cu, Fe, In, K, Mg, Mn, Na, Pb, S, Sb, Se, Zn; JCU AAC).

## 2.4 Results

### 2.4.1 Waste dump material

#### *Primary mineralogy*

Waste dump materials are chemically and mineralogically heterogeneous. They display major (i.e. >1 wt.%) median concentrations of Fe, Pb and S, minor (i.e. >100 ppm) As, Bi, Cu, Sb, Mn, Sn and Zn, and traces (i.e. <100 ppm) of Cd, Co, In, Se and W (Table 2.1) (complete geochemical results in Appendix A2). Such element distributions are consistent with the occurrence of relatively abundant sulphide minerals. Unweathered sulphide-bearing rocks are composed of major quartz (75-95 vol.%), dickite (<1-10 vol.%), illite (<1-10 vol.%), galena (<1-10 vol.%), tetrahedrite (<1-8 vol.%), sphalerite (<1-6 vol.%), chalcopyrite (<1-5 vol.%), and pyrite (<1-4 vol.%) as well as minor to trace amounts (<1 vol.%) of arsenopyrite, bournonite, cobaltite, stibnite, stannite,

sternbergite, cassiterite and wolframite (Table 2.2) (complete SIROQUANT results and summary of XRD results in Appendix A4). Some of the sulphide minerals contain variable amounts of trace elements as indicated by qualitative electron microprobe analyses (tetrahedrite: Ag, As; galena: Ag, Se, W; sphalerite: Cd, In; wolframite: Se) (representative EDS traces in Appendix A4).

**Table 2.1.** Geochemistry of Montalbion mine waste (n = 12).

Element	Maximum	Minimum	Arithmetic Mean	Median
Ag	780	30	293	235
As	6190	153	2230	1900
Bi	1250	<5	229	51
Cd	113	<5	39	21
Co	26	<5	13	11
Cu	35400	34	6920	1850
Fe	10.9	1.71	5.33	5.36
In	90	5	34	20
K	1.23	0.2	0.72	0.74
Mg	0.21	0.03	0.06	0.04
Mn	1670	31	197	51
Na	0.1	0.01	0.02	0.02
P	1860	143	656	526
Pb	69300	9700	29400	25450
S	3.71	1.01	2.23	2.18
Sb	7660	117	2200	768
Se	280	2.1	64	37
Sn	2450	28	457	254
W	80	<5	28	18
Zn	18600	360	6190	4040
paste pH	6.1	2.7	4.2	4.5

All values with the exception of Fe, K, Mg, Na and S (wt.%) are given in ppm dry weight; n - number of samples analysed.

### *Secondary mineralogy*

Sulphidic dump materials are partly or completely oxidised with the development of secondary sulphides, oxides, hydroxides, arsenates and sulphates (Table 2.2) (summary of XRD results in Appendix A4). The Montalbion sulphide lodes were extensively weathered prior to mining, forming abundant secondary minerals (Dash et al., 1991). In addition, post-mining

**Table 2.2.** Minerals identified in the Montalbion mine wastes. Relative solubility in neutral pH water at ambient conditions is shown for secondary post-mining minerals according to Nordstrom and Alpers (1999a), Bigham and Nordstrom (2000), Krause and Ettel (1988), Garvie (1999), Morris (1962) and Nordstrom (pers. comm. 2002).

Paragenetic Order	Name	Formula	
Primary ore mineral	arsenopyrite	FeAsS	
	bournonite	PbCuSbS <sub>3</sub>	
	cassiterite	SnO <sub>2</sub>	
	chalcopyrite	CuFeS <sub>2</sub>	
	cobaltite	(Co,Fe)AsS	
	galena	PbS	
	pyrite	FeS <sub>2</sub>	
	quartz	SiO <sub>2</sub>	
	sphalerite	ZnS	
	stannite	Cu <sub>2</sub> FeSnS <sub>4</sub>	
	sternbergite	AgFe <sub>2</sub> S <sub>3</sub>	
	stibnite	Sb <sub>2</sub> S <sub>3</sub>	
	tetrahedrite	Cu <sub>12</sub> Sb <sub>4</sub> S <sub>13</sub>	
	wolframite	(Fe,Mn)WO <sub>4</sub>	
Secondary pre-mining mineral	chalcocite	Cu <sub>2</sub> S	
	covellite	CuS	
	cuprite	Cu <sub>2</sub> O	
	dickite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	
	goethite	α-FeOOH	
	hematite	α-Fe <sub>2</sub> O <sub>3</sub>	
	illite	KAl <sub>4</sub> (Si <sub>7</sub> AlO <sub>20</sub> )(OH) <sub>4</sub>	
	Secondary post-mining mineral (highly soluble)	chalcanthite	CuSO <sub>4</sub> ·5H <sub>2</sub> O
		gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O
K-alum		KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	
melanterite		Fe <sup>2+</sup> SO <sub>4</sub> ·7H <sub>2</sub> O	
metavoltine		K <sub>4</sub> Na <sub>4</sub> (Fe <sup>2+</sup> ,Zn)Fe <sup>3+</sup> <sub>6</sub> (SO <sub>4</sub> ) <sub>12</sub> O <sub>2</sub> ·20H <sub>2</sub> O	
spangolite		Cu <sub>6</sub> Al(SO <sub>4</sub> )(OH) <sub>12</sub> Cl·3H <sub>2</sub> O	
ramsbeckite		(Cu,Zn) <sub>15</sub> (OH) <sub>22</sub> (SO <sub>4</sub> ) <sub>4</sub> ·6H <sub>2</sub> O	
szomolnikite		Fe <sup>2+</sup> SO <sub>4</sub> ·H <sub>2</sub> O	
tamarugite		NaAl(SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	
Secondary post-mining mineral (relatively insoluble)	anglesite	PbSO <sub>4</sub>	
	antlerite	Cu <sub>3</sub> (SO <sub>4</sub> )(OH) <sub>4</sub>	
	beaverite	PbCuFe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	
	beudantite	PbFe <sup>3+</sup> <sub>3</sub> (AsO <sub>4</sub> )(SO <sub>4</sub> )(OH) <sub>6</sub>	
	brochantite	Cu <sub>4</sub> (SO <sub>4</sub> )(OH) <sub>6</sub>	
	goethite	α-FeOOH	
	jarosite	KFe <sup>3+</sup> <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	
	native sulphur	S	
	osarizawaite	PbCuAl <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	
	plumbojarosite	Pb <sub>0.5</sub> Fe <sup>3+</sup> <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	
	scorodite	FeAsO <sub>4</sub> ·2H <sub>2</sub> O	
	sideronatrite	Na <sub>2</sub> Fe <sup>3+</sup> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>3</sub> ·3H <sub>2</sub> O	
	wroewolfeite	Cu <sub>4</sub> (SO <sub>4</sub> )(OH) <sub>6</sub> ·2H <sub>2</sub> O	

weathering processes have also resulted in the formation of secondary minerals. The distinction of pre- from post-mining secondary minerals is difficult to achieve because some minerals may have formed both prior to and after mining (cf. Lottermoser, 2003). However, post-mining minerals generally occur as mineral efflorescences coating the surfaces of other mineral grains.

At Montalbion, secondary sulphides and some of the sulphate phases (antlerite, brochantite) occur as pervasive replacements of primary sulphide disseminations and veins within the mine wastes. Moreover, some oxides (hematite, cuprite) are present as vein replacements and encrustations on rock surfaces, and minor goethite was identified as thin coatings on rock surfaces and vein replacements. The mineral coatings and efflorescences are regarded as post-mining reaction products, whereas pervasive replacements are thought to be pre-mining weathering phases (Table 2.2).

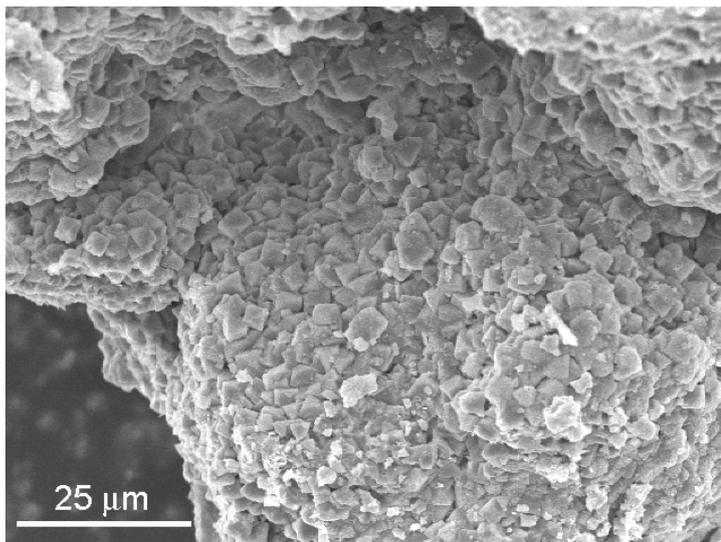
Most of the efflorescent minerals – with the exception of scorodite – are metal and/or alkali sulphates or hydrous sulphates (Table 2.2). Anglesite and plumbojarosite are the most abundant efflorescent minerals, with anglesite comprising up to 9 vol.% and plumbojarosite up to approximately 3 vol.% of the mine waste. An unknown Fe-Sb (oxy)hydroxide/oxide solid was observed as microscopic coating on quartz and tetrahedrite grains. This phase may represent either, (a) goethite with significant adsorbed Sb whereby the acidic pore waters caused the adsorption of anionic species such as  $\text{SbO}_3^-$  (Smith, 1999); or, (b) an oxidation product of tetrahedrite such as senarmonite ( $\text{Sb}_2\text{O}_3$ ), cervantite ( $\text{Sb}_2\text{O}_4$ ) or tripuhyite ( $\text{FeSb}_2\text{O}_6$ ) (Yakhontova et al., 1980), though no discrete Sb or Sb-Fe oxides could be identified.

The efflorescent minerals commonly occur close to their respective parent sulphides. For example, anglesite coats galena-rich mine wastes and chalcantite occurs on chalcopyrite-rich rocks. Rocks containing a polyminerallic sulphide mineralogy are coated by polymetallic sulphates such as osarizawaite and beaverite. The efflorescences thereby display a wide range of habits, and the forms and faces of the efflorescences appear to be related to their solubility. Relatively insoluble minerals (e.g. anglesite, plumbojarosite,

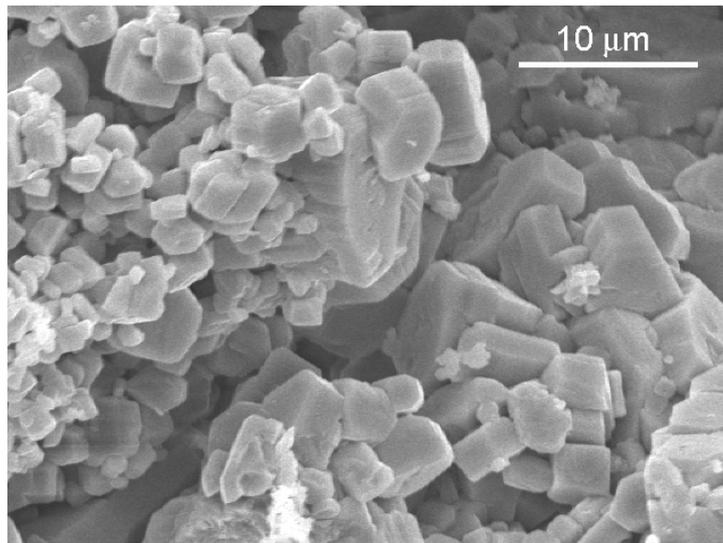
beaverite,



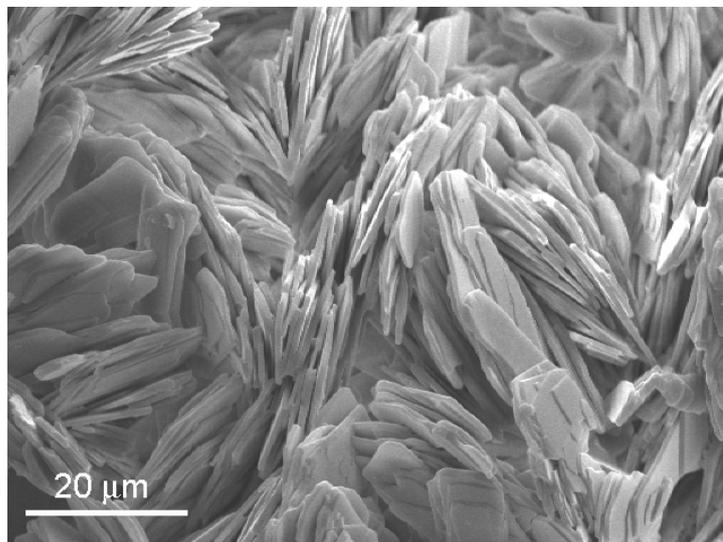
**Figure 2.2a.**



**Figure 2.2b.**



**Figure 2.2c.**



**Figure 2.2d.**

**Figure 2.2.** Montalbion waste dump materials. (a) Rio Tinto mine waste dump viewed from its top. Note the steepness of the site and the unconsolidated nature and heterogeneous grain size of the waste material. (b) to (d) SEM micrographs of (b) osarizawaite, (c) chalcantinite, and (d) tamarugite. These post-mining secondary sulfate minerals occur as encrustations (b) and floury dustings (c, d) on waste rock surfaces.

osarizawaite) occur as subhedral granular masses that form earthy surface encrustations (Fig. 2.2b). In contrast, highly soluble efflorescences (e.g. melanterite, chalcantinite, tamarugite) are present as euhedral grains in floury dustings on rock and adit surfaces (Fig. 2.2c,d). This behaviour is likely

attributed to the complete dissolution and removal of highly soluble minerals during rainfall events and re-precipitation of new crystals during dry periods.

### *Laboratory experiments*

Most waste rock dump samples contain visible sulphides with modal amounts varying from <1 vol.% to 20 vol.%. It is therefore assumed that much of the total sulphur is present as sulphide S and to a lesser degree as sulphate S. Paste pH measurements of milled mine wastes confirm the fact that the waste is acid (average pH value of 4.2, Table 2.1). Hence, the net acid producing potential (NAPP) of these materials is high. On the other hand, dump materials have a low acid neutralisation capacity (ANC) due to the lack of carbonate and the abundance of quartz, dickite and illite.

The immersion of mine wastes into distilled water for one day produced low pH, high conductivity leachates (pH: 2.67-3.86; conductivity: 384-990  $\mu\text{S/cm}$ ) (complete results in Appendix A5). Leachates collected after one week and one month generally had higher pH and lower conductivity concentrations (pH: 2.89-4.66; conductivity: 257-542  $\mu\text{S/cm}$ ). Furthermore, considerable concentrations of metals (Al, Cu, Fe, Pb, Zn), metalloids (As), alkalis (Ca, Mg, Na, K), and sulphur (presumably present as sulphate) were detected in the solutions. Metal values were as high as 108 mg/l Cu, 40 mg/l Zn, 25 mg/l Fe, 12.5 mg/l Pb, and 374 mg/l  $\text{SO}_4$ . Generally, concentrations of most elements decreased with immersion time. Lead was a notable exception with leachate values increasing or remaining unchanged with immersion time. The abundance of soluble mineral efflorescences in the wastes and the relatively high concentrations of sulphate, metals and alkalis in the leachates suggest that the dissolution of sulphate efflorescences accounts for much of the detected leachate chemistry. A small amount of metal desorption from clay minerals and Fe (oxyhydr)oxides as well as sulphide oxidation and consequent metal release may have occurred, particularly when the water was removed and replaced between experiment stages. However, the complete immersion of the waste in stagnant distilled water would not have allowed primary and secondary sulphide oxidation to

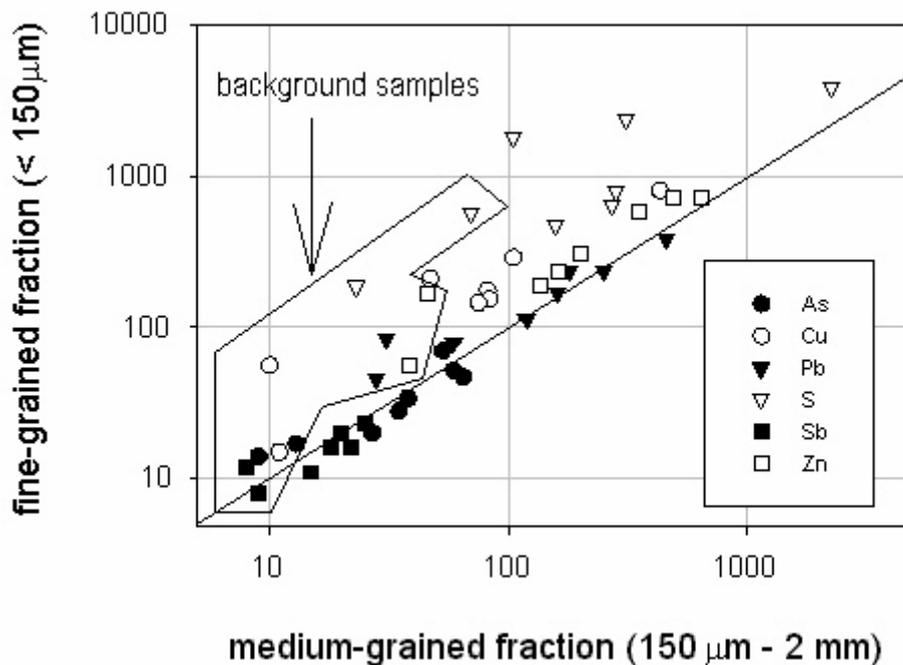
proceed at a significant rate. Thus, the wetting of Montalbion mine wastes produces acidic “first flush waters” characterised by elevated sulphate and metal values (Cu, Zn, Fe). These element loads are due predominantly to the dissolution of secondary alkali and metal sulphate salts.

#### 2.4.2 Stream sediments

Oakey Creek stream sediments in the Montalbion area range from very immature materials (gravel to cobble size), through sands to silts and muds deposited in low-energy settings. The sediments are dominantly composed of metasediment-derived detrital quartz with minor illite and rutile. Many stream sediments in the mine area and immediately downstream contain mineralised detritus (e.g. sulphidic vein material), Fe-rich precipitates (i.e. “yellow-boy”) and efflorescent salts.

Two stream sediment samples collected upstream of the mine area are considered to represent background sample material and their fine-grained (<150 µm) and medium-grained (150 µm - 2 mm) fractions have relatively low S and low metal and metalloid contents (Fig. 2.3) (complete results in Appendix A2). Mining influenced stream sediments contain distinctly higher element concentrations (Fig. 2.3). Sulphur and metal enriched sediments (i.e. median of 4 samples; <150 µm size fraction; As: 34 ppm; Cu: 289 ppm; Fe: 2.9 wt.%; In: 1.5 ppm; Pb: 169 ppm; S: 789 ppm; Sb: 20 ppm; Zn: 306 ppm) particularly occur in the mining area up to 500 m downstream. The highest As, Cu, Fe, In, S, Sb and Zn concentrations occur in fine-grained sediments (<150 µm) 50 m downstream of the mine site. Moreover, the fine-grained (<150 µm) fraction of the stream sediment population influenced by mining displays distinctly higher S, Cu and Zn concentrations than the medium-grained (150 µm - 2 mm) fraction (Fig. 2.3). In contrast, As, Pb and Sb concentrations are similar in both size fractions. This latter element distribution in the mining influenced population is interpreted as reflecting the importance of chemical dispersion of metalloids (As, Sb) in the Montalbion area. Furthermore, there are correlations of log-transformed data, in particular of Fe with As and Sb in the fine-grained (<150

$\mu\text{m}$ ) fraction and of S with Cu, In and Zn in the medium-grained ( $150\ \mu\text{m}$  -  $2\ \text{mm}$ ) fraction. The Fe-As-Sb correlation is interpreted to represent the preferential adsorption/co-precipitation of dissolved As and Sb onto/with Fe-rich precipitates from acidic waters (Smith, 1999). The correlation of S with In and Zn is interpreted to represent the association of In and Zn with sphalerite. The latter element distribution highlights the fact that active erosion of waste dump materials leads to the physical dispersion of larger ore particles (e.g. sphalerite) into local stream sediments.



**Figure 2.3.** Geochemistry of Oakey Creek sediments. The concentrations of selected elements have been plotted for the fine- and medium-grained fractions of the background and mining influenced populations. The line indicates equal concentrations of elements in both size fractions.

#### 2.4.3 Waters

Surface waters within the Montalbion area show a range of element concentrations (Bartereau et al., 1998). Elements carried in solution in significant quantities ( $>100\ \mu\text{g/l}$ ) are Al, Cd, Co, Cu, Fe, Mn, Ni and Zn.

Drainage waters from the Rio Tinto waste dump and Oakey Creek surface waters immediately downstream of the AMD inflow have the lowest pH (3.3) and highest sulphate (596 000 µg/l) and metal values (Table 2.3) (complete water chemistry results in Appendix A3).

During dry periods, the acidic waters of Oakey Creek are gradually neutralised, most likely due to buffering reactions with stream sediments. The waters reach a pH value of 4.8 approximately 0.5 km downstream of the mine site. Surface water at this location evaporates and/or enters the baseflow of the stream. Stream waters taken at distances up to 0.5 km from the mine site remain elevated in metal contents (Al, Cd, Co, Cu, Fe, Mn and Zn) (Table 2.3).

The lack of rainfall at the field site during 2001 – 2002 prevented the sampling of Oakey Creek during periods of flow. Background Oakey Creek water was collected upstream from the mine site during moderate flow by Barterreau et al., (1998). These waters have detectable Fe (1100 µg/l), Cu (150 µg/l) and Zn (90 µg/l) at a pH of 7.5 (Appendix A3). These waters are enriched in metals because the study area is part of the Herberton mineral province with over 3000 mineral occurrences and naturally high background metal concentrations. During moderate flow, drainage waters from the Rio Tinto waste dump add significant acid, metal-rich waters to Oakey Creek (pH 4.1, 77 000 µg/l Al, 700 µg/l Cd, 380 µg/l Co, 20 000 µg/l Cu, 8900 µg/l Fe, 14 000 µg/l Mn, 240 µg/l Ni, 300 µg/l Pb, 80 000 µg/l Zn) (Barterreau et al., 1998) (Appendix A3). During moderate flow the stream waters are gradually neutralised, most likely due to buffering reactions with stream sediments and mixing with more alkaline waters. The waters reach a pH value of 6.4 approximately 1 km downstream of the mine site. Anomalous Zn concentrations (up to 1600 µg/l) are detectable in neutral pH waters up to 2 km downstream (Barterreau et al., 1998). After heavy rainfall coupled with extraordinary flow and dilution, Oakey Creek waters within the mining area display pH values (7.5) and Fe and Cu concentrations (400 µg/l and 150 µg/l, respectively) which are at or below background levels (Qld NRM, unpub. data) (Appendix A3). However, Al (550 µg/l), Cd (3.1 µg/l) and Zn (560 µg/l) concentrations remain above background levels despite the dilution.

**Table 2.3.** Water quality analyses of Oakey Creek

Parameter	April 2002		
	0 m	50 m	500 m
Distance downstream from mine input	0 m	50 m	500 m
Generals			
pH	3.42	3.30	4.79
Conductivity ( $\mu\text{S}/\text{cm}$ )	1438	1294	859
TDS (mg/l)	811	792	541
Hardness (mg/l as $\text{CaCO}_3$ )	374	211	308
Alkalinity (mg/l as $\text{CaCO}_3$ )	<0.1	<0.1	1.3
Major ions (mg/l)			
Na	9.8	8.6	28
K	7.3	8.3	7.5
Ca	92	45	69
Mg	35	24	33
$\text{SO}_4^{2-}$	525	596	362
Cl	10	8.3	7.5
$\text{HCO}_3^-$	<0.1	<0.1	1.6
Trace metals ( $\mu\text{g}/\text{l}$ )			
Ag	0.5	0.5	0.5
Al	27700	27600	868
As	3	1	2
Ba	81	45	126
Be	8	8	<0.1
Cd	561	383	76
Co	273	222	59
Cr	<1	<0.1	<0.1
Cu	12900	5430	288
Fe	12100	11200	372
In	0.4	0.4	0.3
Mn	18500	11900	9870
Mo	<0.1	<0.1	<0.1
Ni	172	133	25
Pb	52	67	36
Sb	0.2	0.1	2
Se	<1	<1	<1
Zn	60700	45600	13100

Computational modelling (PHREEQC2) was conducted on water samples collected during a period of no flow (complete results in Appendix A3). The results indicate that the drainage waters emanating from the Rio Tinto waste dump are oversaturated with respect to alunite and barite. Oakey Creek waters – taken distal to the drainage water input – are oversaturated with alunite and barite as well as gibbsite, goethite and hematite pointing to evaporation and mineral precipitation processes in the streambed. However, such computational modelling provides only limited information on the chemical status of AMD

waters due to the lack of thermodynamic data on phases typically found in AMD environments (e.g. sulphates, schwertmannite), inevitable disequilibrium within the waters and the effect of biotic processes on mineral precipitation.

#### 2.4.4 Streambed precipitates

Mineral precipitates were observed in the Oakey Creek stream bed (Fig. 2.4a,b) and include the following: (a) ochreous, yellow-red-brown precipitates in stagnant water pools, between pool ripples, and on creek banks where AMD waters enter the stream; (b) cream-green/blue, yellow and white efflorescent salts present at the edge of stagnant water pools; and (c) metallic copper coloured precipitates on a concrete pipe which subsequently proved to be mixtures of botryoidal tenorite and microcrystalline cuprite.

##### *Ochres*

The ochreous precipitates occur as yellow-brown (Munsell colour value 7.5YR 5/8), honeycombed encrustations (i.e. schwertmannite and amorphous Fe-oxyhydroxides) (representative XRD trace in Appendix A6), dark red-brown (2.5YR 4/8) concretions (i.e. schwertmannite and goethite), and yellow-brown (10YR 6/6) flocculant precipitates (i.e. goethite). Schwertmannite displays two major habits; the characteristic “pin-cushion” morphology of radiating fibrous crystals (Fig. 2.4c) (cf. Bigham et al., 1994); and hollow tubes of radiating crystals which produce the honeycomb appearance to the naked eye (Fig. 2.4d). The latter texture may be due to the precipitation of schwertmannite onto plant roots that have since decayed. Goethite displays a subhedral rod-like morphology commonly observed in mine drainage precipitates (Bigham, 1994).

Geochemical analyses of selected ochres show that the schwertmannite-amorphous Fe-oxyhydroxide and schwertmannite-goethite mixtures contain appreciable amounts of Al, As, Cu, In, Fe, Mn, S, Pb and Zn (complete ICP-MS results in Appendix A6). Compared with Oakey Creek water collected from the same site, both types of ochreous precipitates show preferential enrichments in Fe, As and Sb (Fig. 2.5). The schwertmannite-amorphous Fe-oxyhydroxide

precipitates also show preferential enrichment in In (Fig. 2.5). In contrast, surface waters are relatively enriched in Al, Cd, Cu, Mn and Zn. The preferential precipitation of As and Sb into the ochreous precipitates reflects coprecipitation and pH dependent metal adsorption (cf. Smith, 1999) and is in agreement with concentration processes previously established from AMD environments (Fuge et al., 1994; Carlson et al., 2002; Ashley et al., 2003). In contrast, there is no previous knowledge on the behaviour of In in acid surface waters. However, the relative In enrichment detected in the ochreous precipitates suggests that the element is preferentially adsorbed to Fe oxyhydroxides and Fe hydroxysulphates under low pH conditions.

### *Mineral efflorescences*

Efflorescent salts occur as globular aggregates comprising fine-grained acicular and prismatic crystals (Fig. 2.4d,e). Identified efflorescences include hydrous alkali and metal sulphates (Table 2.4) (summary of XRD results in Appendix A6). Geochemical analyses of selected efflorescences reflect the chemistry of Oakey Creek waters (Fig. 2.5). X-ray diffraction patterns of the most abundant phase correspond to apjohnite ( $\text{MnAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ; powder diffraction file No. 29-886) (representative XRD traces in Appendix A6). However, semi-quantitative electron microprobe analyses of this abundant efflorescent salt returned elemental weight percentages (S>Al>Zn>Mg>Mn>Cu>Ca) (Appendix A6) that clearly do not match the apjohnite composition. Extensive solid solution is known to occur between halotrichite ( $\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ), pickeringite ( $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ), and apjohnite ( $\text{MnAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ) (Jambor et al., 2000). Hence, the efflorescent salt from Montalbion is likely a member of the dietrichite–pickeringite–apjohnite series rather than pure apjohnite. The apjohnite JCPDS powder diffraction file is based on the work of Menchetti and Sabelli (1976), who provided only a partial mineral chemical analysis. This type material may contain elements other than Mn and therefore, the JCPDS powder diffraction file of apjohnite needs to be refined.



Figure 2.4a.

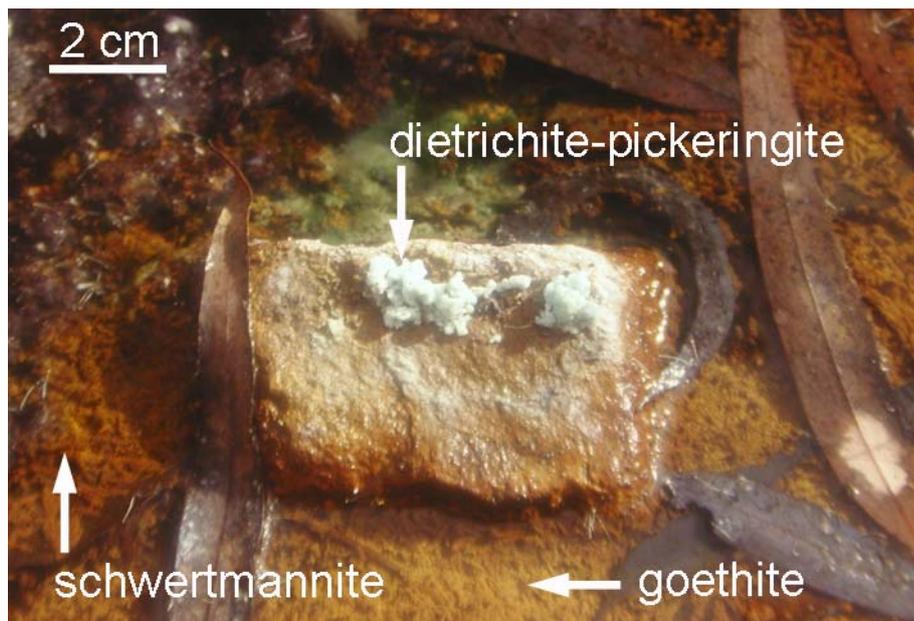
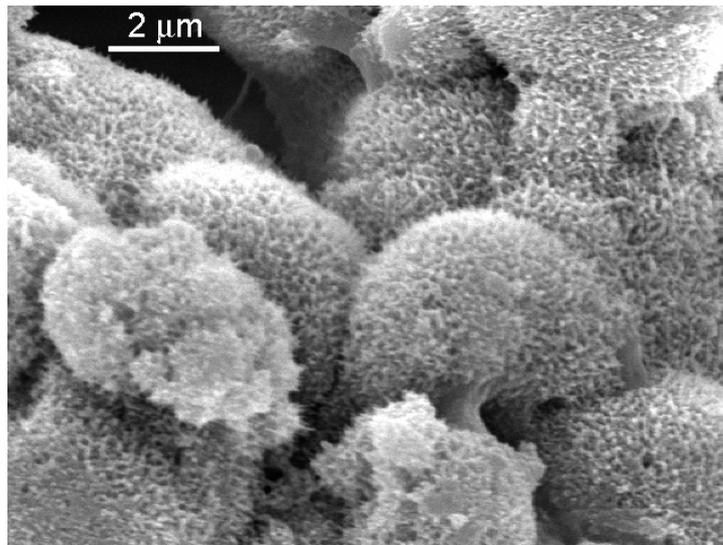
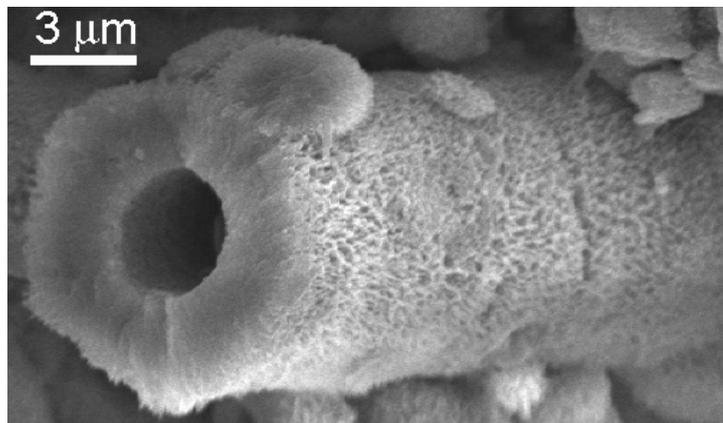


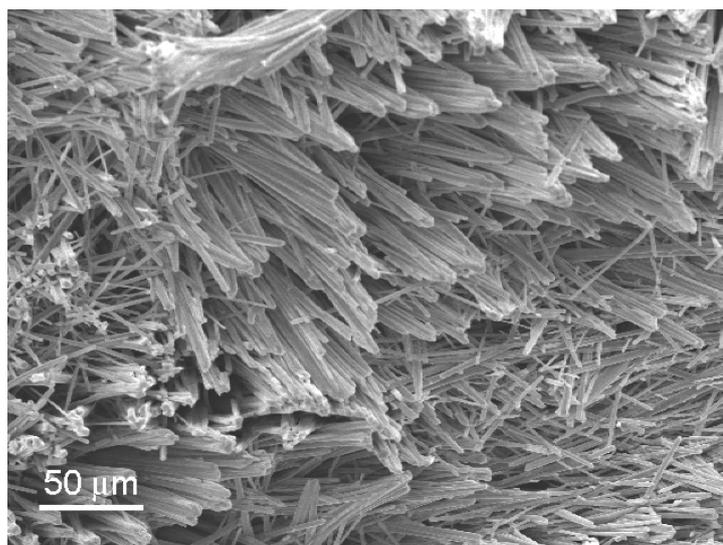
Figure 2.4b.



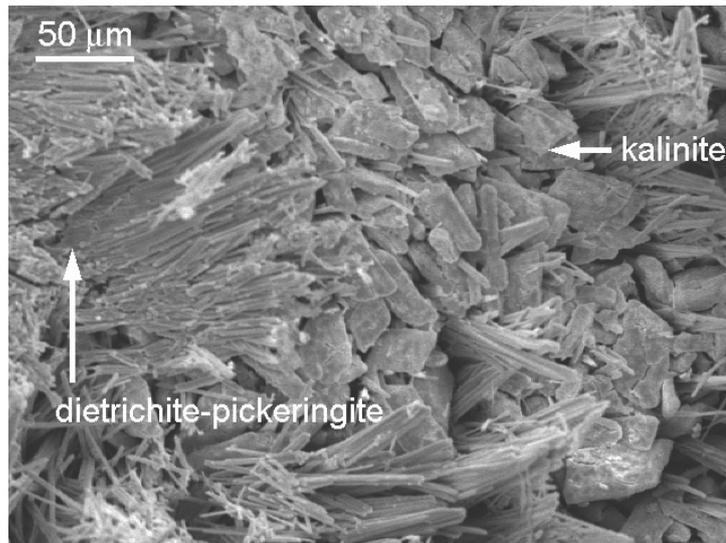
**Figure 2.4c.**



**Figure 2.4d.**



**Figure 2.4e.**



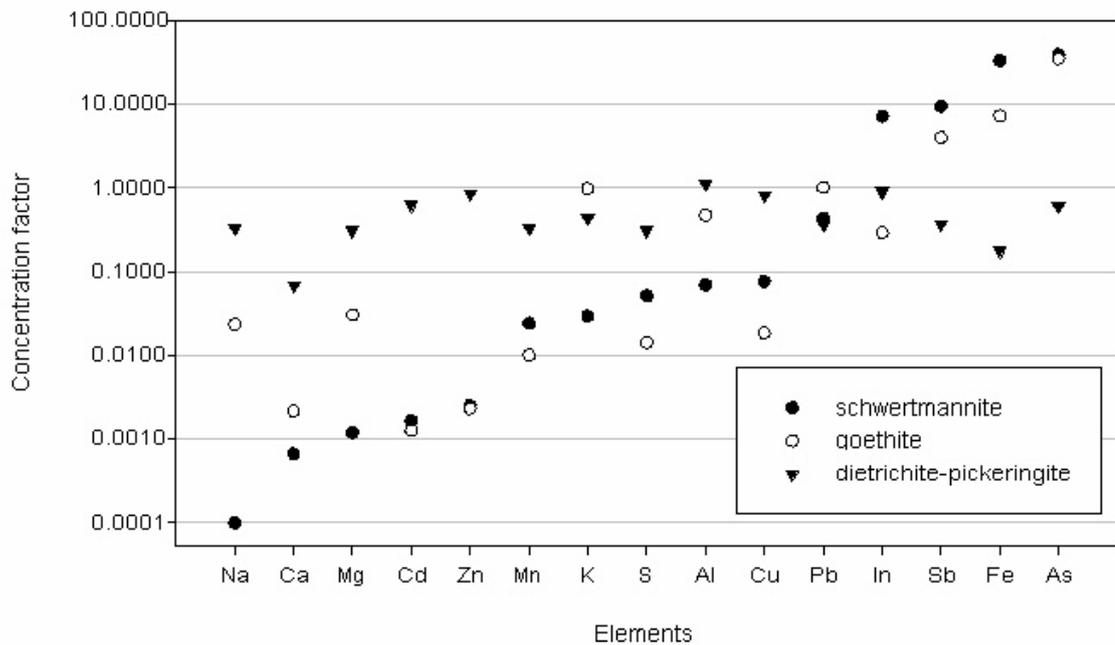
**Figure 2.4f.**

**Figure 2.4.** Mineral efflorescences and ochreous precipitates in Oakey Creek. (a) Oakey Creek stream bed below the drainage inflow. (b) Detail of streambed showing major efflorescent and precipitate phases. SEM photographs: Schwertmannite (sample OCE4) showing (c) the characteristic pin-cushion texture and (d) a hollow tubular texture. Mineral efflorescences (sample OCE8) (e) Dietrichite-pickeringite showing acicular texture. (f) Kalinite showing prismatic texture intermixed with dietrichite-pickeringite.

## 2.5 Discussion

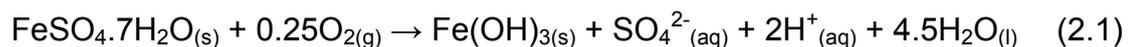
### 2.5.1 AMD generation and first flush waters

Much of the research into AMD development at mine sites has been related to the oxidation of sulphides. This previous research has shown that the oxidation of Fe-bearing sulphides, especially pyrite and pyrrhotite, leads to the production of acidic, metal laden drainage waters. At Montalbion, the mine waste generally contains <1 vol.% pyrite, yet the chemistry of mine drainage waters and static and kinetic test data clearly indicate that the waste is acid generating. Although the relatively low concentration of pyrite may still generate substantial acid, several other mineral reactions are also likely responsible for the acid production. Firstly, Montalbion mine waste contains major amounts of chalcopyrite, Fe-bearing sphalerite and tetrahedrite, and their oxidation also generates acid (Yakhontova et al., 1980; Jennings et al., 2000). Secondly, the



**Figure 2.5.** Concentration factors of mineral efflorescences (diétrichite-pickeringite) and ochreous precipitates (schwertmannite, goethite) from Oakey Creek. The concentration factor is the ratio of the element concentration in the solid to the element concentration in Oakey Creek water. The elements are ordered so that element concentration factors in the ochres increase from the left to the right of the diagram.

waste contains abundant highly soluble efflorescences, some of which will generate acid upon their oxidative dissolution. The  $\text{Fe}^{2+}$ -bearing minerals melanterite, metavoltine and szomolnikite, and the  $\text{Al}^{3+}$ -bearing minerals K-alum, spangolite and tamarugite produce acidity upon their dissolution due to the hydrolysis of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , respectively (Cravotta, 1994; White et al., 1999; Jambor, 1994; Jambor et al., 2000; Frau, 2000). For example, melanterite may dissolve as follows (Frau, 2000):



Moreover, the release of  $\text{Fe}^{2+}$  into water and its oxidation to  $\text{Fe}^{3+}$  do not necessarily result in the precipitation of Fe-hydroxides. Available  $\text{Fe}^{3+}$  can also trigger more sulphide oxidation (Keith et al., 1999; Alpers and Nordstrom, 1999; Plumlee, 1999).

**Table 2.4.** Stream bed precipitates identified in the AMD affected Oakey Creek.

Mineral	Formula
<i>major</i>	
schwertmannite	$\text{Fe}_8\text{O}_8(\text{SO}_4)(\text{OH})_6$
goethite	$\text{Fe}(\text{OH})_3$
diétrichite- pickeringite- apjohnite type phase	$(\text{Zn},\text{Mg},\text{Mn})\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
kalinite	$\text{KAl}(\text{SO}_4)_2 \cdot 11\text{H}_2\text{O}$
melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
<i>minor</i>	
chalcantite	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
kroehnkite	$\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$
zaherite	$\text{Al}_{12}(\text{SO}_4)_5(\text{OH})_{26} \cdot 20\text{H}_2\text{O}$
<i>trace</i>	
aluminite	$\text{Al}_2\text{SO}_4(\text{OH})_4 \cdot 7\text{H}_2\text{O}$
alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$
bonattite	$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$
cuprite	$\text{Cu}_2\text{O}$
epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
gunningite	$(\text{Zn},\text{Mn})\text{SO}_4 \cdot \text{H}_2\text{O}$
gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
pentahydrate	$\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$
picromerite	$\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
rostitite	$\text{AlSO}_4(\text{OH},\text{F}) \cdot 5\text{H}_2\text{O}$
tenorite	$\text{CuO}$

Thirdly, desorption of  $\text{H}^+$  from the surfaces of secondary sulphates and clays may also contribute significant acidity to drainage waters. Finally, the lack of suitable acid neutralising minerals in the Montalbion waste allows the unhindered production of acidic, metal-rich drainage waters. The abundance of illite and dickite is low, their reaction kinetics are slow and the minerals provide only limited acid neutralisation and buffering at a pH plateau of 3.5 to 4.1 (Plumlee, 1999; Stromberg and Banwart, 1999; Jambor et al., 2002). Thus, at Montalbion, pronounced AMD generation is due to the combination of sulphide oxidation, dissolution of acid generating mineral efflorescences and limited buffering from gangue phases. Mineral efflorescences with low solubility (anglesite, plumbojarosite, scorodite, antlerite, brochantite) retain Pb and minor As and Cu in the waste dump, whereas readily soluble minerals (melanterite,

chalcantite) release Fe, Zn and Cu to pore and drainage waters. Hence, during rainfall events, minerals with low solubilities become enriched on rock surfaces as the highly soluble minerals are removed. The mineral dissolution experiments also illustrate that first flush drainage waters are enriched in Fe, Zn, Cu and sulphate, with these ions being derived from the dissolution of mineral efflorescences. Rapid depletion of the highly soluble efflorescences results in a decrease in metal and sulphate leachate concentrations with ongoing flushing.

The generation of drainage waters from sulphidic mine wastes in a seasonally wet climate is controlled by wetting and drying cycles (Perkins et al., 1997). Waste piles are intermittently wetted by meteoric water and run-off; they are dried by drainage and evaporation (Perkins et al., 1997). In the case of partly oxidised mine waste with high concentrations of secondary minerals like Montalbion, intense wetting of these materials will release temporarily stored acidity and metals from soluble secondary minerals and produce first flush waters of significant acidity, salinity and metal content. These mobilised elements and compounds may become permanently or temporarily stored downstream from the waste in ochreous precipitates or evaporative mineral efflorescences coating local streambeds.

### 2.5.2 AMD into receiving stream

At Montalbion, low pH (3.3-4.1) sulphate- and metal-rich waters emanate from the mine site and upon oxygenation precipitate Fe-rich ochres in the Oakey Creek bed (Fig. 2.4a,b). The prevalent pH and hydrochemical conditions favour the formation of schwertmannite and goethite (Bigham et al., 1996b). Adsorption and coprecipitation processes account for the preferential As-Sb-In enrichment of secondary Fe minerals (cf. Carlson et al., 2002; Ashley et al., 2003). Relative metal concentration factors of these ochres ( $Pb > Cu > Zn > Cd$ ; Fig. 2.5) agree well with the metal sorption curves of Smith (1999). The resulting water chemistry is characterised by elevated sulphate, alkali, Al, Zn, Cu, Mn, Fe and Cd concentrations. During the dry season, evaporative concentration of solutes occurs, resulting in the precipitation of efflorescences.

During heavy rainfall events, flushing of the creek bed with neutral pH water results in dissolution of the soluble efflorescent salts and consequent metal remobilisation and transport downstream, particularly of Zn and Cd.

Indium is a trace element of many sulphide ores and is commonly hosted by sphalerite (Schwarz-Schampera and Herzig, 2002). Although many In-bearing sulphide ores are AMD generating, the behaviour of In in acidic surface waters is largely unknown. At Montalbion, waste rocks (In/Zn ratios: ~1/180) release In to AMD waters through the oxidative dissolution of sphalerite. The seepage waters enter Oakey Creek where In is preferentially incorporated into the ochreous streambed precipitates leading to exceptionally low In/Zn ratios in Oakey Creek waters (~1/150000). Thus, In adsorption onto and coprecipitation with Fe oxyhydroxides and hydroxysulphates cause In attenuation in acidic waters.

## 2.6 Conclusions

The Montalbion mining area contains several waste dumps located on steep slopes which are actively eroding and are subject to dynamic landsliding. The waste dumps are mineralogically and geochemically heterogeneous with high concentrations of Fe, Pb and S, minor As, Bi, Cu, Mn, Sb, Sn and Zn, and traces of Cd, Co, In, Se and W. The unweathered waste dump mineralogy consists of major quartz (75-95 vol.%) with subordinate clay and sulphides (1-10 vol.%) (galena, tetrahedrite, sphalerite, chalcopyrite, pyrite). Extensive weathering of the sulphide minerals, both prior to and post-mining, has resulted in the formation of abundant secondary metal and/or alkali (hydrous) sulphates. Post-mining efflorescences generally occur as thin encrustations or floury dustings on other mineral grains.

Ephemeral AMD from the Montalbion mining area runs into Oakey Creek resulting in acidic (pH 3.3-4.1) surface waters with elevated sulphate and Al, Cd, Co, Cu, Fe, Mn, Ni and Zn concentrations throughout the year, except during periods of heavy rainfall and resulting extraordinary stream flow in Oakey

Creek. The generation of AMD at Montalbion is probably caused by a combination of sulphide (chalcopyrite, sphalerite, tetrahedrite, pyrite) oxidation, the dissolution of  $\text{Fe}^{2+}$ - and  $\text{Al}^{3+}$ -bearing secondary sulphate efflorescences, the desorption of  $\text{H}^+$  from mineral surfaces, and a paucity of acid neutralising minerals. Upon entering Oakey Creek, oxygenation of the AMD promotes Fe precipitation, resulting in extensive “yellow-boy” formation (amorphous Fe, schwertmannite, and goethite) on the streambed. Evaporation of Oakey Creek waters during dry periods leads to the precipitation of efflorescent hydrous metal and alkali sulphates. Geochemical analyses of the Fe-rich precipitates reveal preferential concentration of As, Sb and In into the ochres through adsorption/coprecipitation processes with Fe hydroxides and hydroxysulphates.

The wetting/drying cycle of the tropical climate has an important control on the chemistry of both the mine drainage and Oakey Creek waters. During dry periods, evaporation leads to the formation of soluble efflorescent mineral salts on the waste dump and on the edges of stagnant pools in Oakey Creek. Rainfall events dissolve the highly soluble efflorescences in the waste dump resulting in acidic “first flush” drainage waters with elevated sulphate, Fe, Cu and Zn. Less soluble efflorescent phases retain Pb and As in the waste rock. Continuing heavy rainfall flushes Oakey Creek with neutral pH waters dissolving the efflorescences on the streambed, remobilising sulphate, Al, Cd, Cu, Mn and Zn.

Chemical characteristics of ephemeral drainage waters from mine sites in tropical climates can vary greatly during different seasons. An important control on drainage water chemistry is the speciation and solubility of secondary efflorescent minerals developed in mine site environments.